

# **Rapid On-Site Environmental Sampling and Analysis of Propellant Stabilizers and their Decomposition Products by Portable Sampling and Thin-Layer Chromatography Kits**

*J.S. Haas, M.A. Gonzalez*

This article was submitted to  
Chemistry for the Protection of the Environment (CPE XIII)  
Hilo, HI, June 9-12, 2002

**U.S. Department of Energy**

Lawrence  
Livermore  
National  
Laboratory

**August 4, 2003**

## **DISCLAIMER**

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

# Rapid On-Site Environmental Sampling and Analysis of Propellant Stabilizers and their Decomposition Products by Portable Sampling and Thin-Layer Chromatography Kits

Jeffrey S. Haas and Marjorie A. Gonzalez

*Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, CA 94550 USA*

*Phone: 925-423-2363; E-mail: [haas1@llnl.gov](mailto:haas1@llnl.gov)*

*Phone: 925-423-5630; E-mail: [gonzales3@llnl.gov](mailto:gonzales3@llnl.gov)*

## ABSTRACT

Sustainable future use of land containing unexploded ordnance requires extensive field assessments, cleanup, and restoration. The ordnance is generally semi-exposed or buried in pits and, because of aging, needs to be handled with caution. Being able to characterize the ordnance in the field to minimize handling, as well as to distinguish it from inert mock material, greatly facilitates assessments and clean-up.

We have developed unique sample preparation methodologies and a portable thin-layer chromatography (TLC) kit technology for rapid field screening and quantitative assessment of stabilizer content in propellants and, energetic materials (explosives) in environmental scenarios. Major advantages of this technology include simultaneous chromatography of multiple samples and standards for high sample throughput, high resolution, very low detection limits, and ease of operation.

The TLC kit technology, sponsored by the Defense Ammunition Center (DAC) of the U.S. Army, is now patented and has been completely transitioned to our commercial partners, Ho'olana Technologies, located in Hilo, Hawaii. Once fully deployed in the field, the new technology will demonstrate a cost-effective and efficient means for determining the percent of effective stabilizer that is remaining on-site and at munitions clean-up sites, as well as munitions storage facilities. The TLC kit technology is also readily applicable for analysis at military or commercial facilities, for a variety of emergency and non-emergency scenarios, and for situations where public concern is high.

**Keywords:** explosives analysis, field test kit, propellant stabilizer analysis, thin-layer chromatography, defense clean-up, environmental field test kit

## Technical Approach

### Background:

For onsite analysis, the examination of the vast number of samples necessitates the use of quick, reliable, field portable equipment that can rapidly, quantitatively verify the many chemically different types of ammunition, explosives, and pyrotechnics. The most common suite of analytes to detect is large, consisting of very chemically different compounds and usually occurs at trace levels in complex environmental matrices. This suite encompasses smokeless powders, black powders, and numerous propellant and energetic formulations. Detection should also be sought for common decomposition products of these explosives such as the methylanalines, aminonitrotoluenes, nitrotoluenes, mono- and dinitroglycerines, and the nitrobenzenes under on-site conditions.

Selection of on-site analytical techniques involves evaluation of many factors including the specific objectives of this work. Numerous instrumental techniques, GC, GC-MS, GC-MS-TEA, HPLC, HPLC-MS-MS, IR, FTIR, Raman, GC-FTIR, NMR, IMS, HPLC-UV-IMS, TOF, IC, CE, etc., have been employed for their laboratory-based determination. Most, however, do not meet on-site analysis criteria, (i.e., are not transportable or truly field portable, are incapable of analyzing the entire suite of analytes, cannot detect multiple analytes compounded with environmental constituents, or have low selectivity and sensitivity). Therefore, there exists no single technique that can detect all the compounds and there are only a few techniques exist that can be fielded. The most favored, portable, hand-held instrumental technique is ion mobility spectrometry (IMS), but limitations in that only a small subset of compounds, the inherent difficulty with numerous false positives (e.g., diesel fumes, etc.), and the length of time it takes to clear the IMS back to background are just two of its many drawbacks.

While conventional TLC analysis is not considered an instrumental technique, it is routinely used in analytical laboratories worldwide for semi-quantitative and qualitative characterization of unknowns. This laboratory-based technique is ideal for rapid screening, is highly sensitive, and is selective for the identification of analytes sought. Analytes commonly detected in complex samples are explosives, drugs, plant extracts, pesticides, counterfeit inks, plasticizers, and many other types of organics, organometallics, and propellant stabilizers.

Unlike column chromatography approaches that can only process single samples sequentially, one TLC plate can accommodate and analyze multiple samples and standards. Numerous samples are processed simultaneously in a unique solvent tank, separating out the stabilizer or explosive analyte(s) away from the sample matrix. Semi-quantitative assessments with nanogram detection limits are readily obtained by inspection of the plates. This process allows numerous samples to be analyzed by a single operator per day.

Once the chromatography is complete, only the resolved propellant stabilizer or explosive components appearing as separated spots on the TLC plate can be further enhanced with a unique reagent (See Figure 1). Quantitative analysis and data archival may be performed using an illumination box, camera, and data acquisition equipment as described later. The major advantage of this technology is simultaneous chromatography of multiple samples and standards, extremely low detection limits, potential for quantitation, and its simplicity to operate. Once implemented, the new technologies will be very cost-effective, fast, and efficient for low nanogram detection of propellant stabilizer compounds on-site at military and former military training ranges in a variety of emergency and non-emergency scenarios.

## Single Method for All Propellant Formulations

- Spot and location indicates stabilizer type
- Spot size and density indicates amount

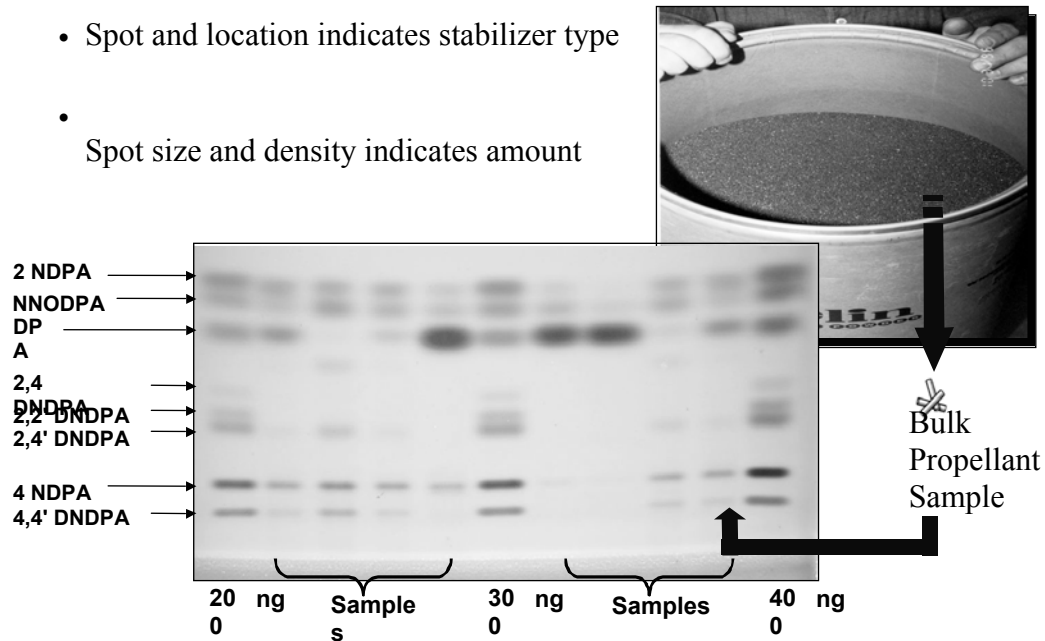
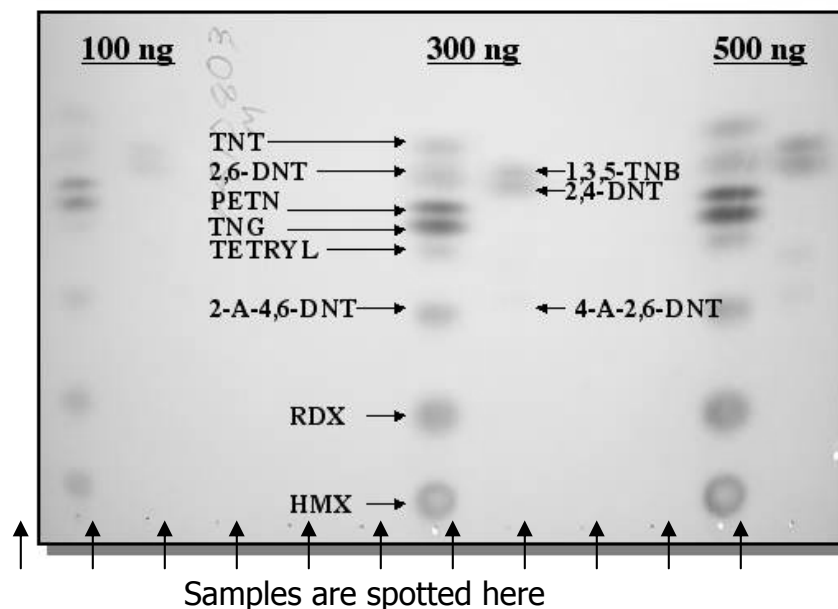


Figure 1

TLC is also one of the analytical techniques that is commonly used to support evidence in courts of law. The chemistry concept for visualization is not unique since this reaction scheme, converting explosive to pink dyes, is decades old. TLC provide rapid screening capability for the presence of a broad range of explosive residues. TLC also provides a means for obtaining specificity, i.e., identifying numerous types of explosives, their concentrations, and also provides the capability to ratio the amounts of the explosives present. For example, Comp B has a mixture of RDX and TNT in its formulation, and if present in the sample the ratio would be 60:40, respectively. This ratio becomes visually apparent by the density of the spots with TLC technology (See Figure 2).

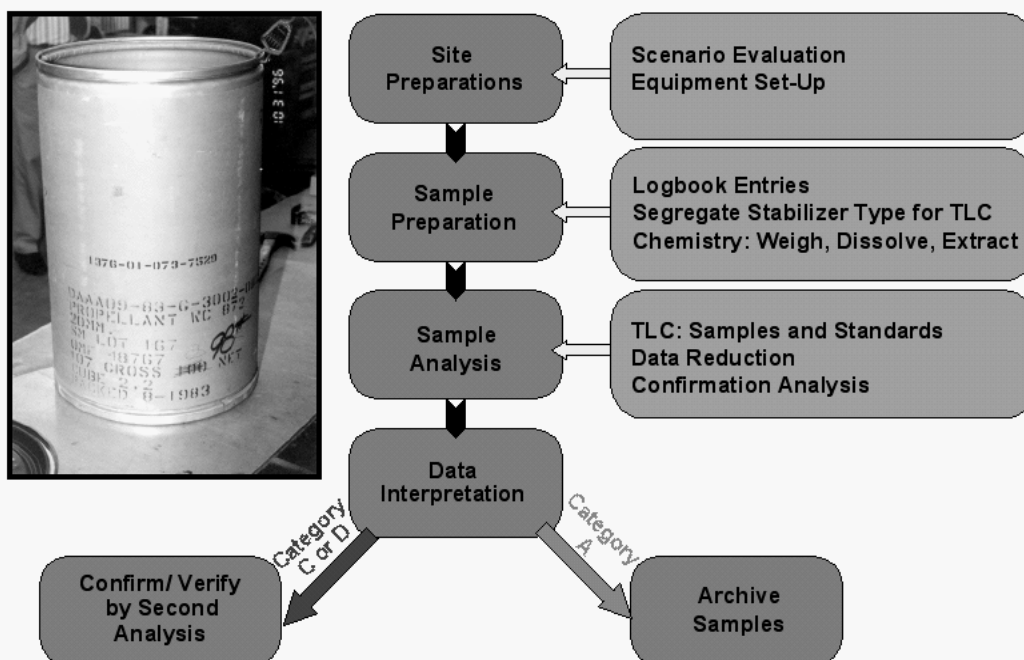


**Figure 2**

In Figure 2 above, the three columns of spots are actually three sets of common explosives one may encounter in a very complex sample. For clarity in this picture, only the center column of spots was labeled. Each spot, i.e., each explosive migrates up the TLC plate away from where it was originally spotted, up to a location on the TLC plate that is unique for that particular explosive. HMX is the first spot at the bottom; next one up is RDX, and so on. The density of the spot is related to its concentration. To further show the density, each explosive set was spotted at three different concentrations, the lowest on the left and the highest on the right from left to right at 100, 300, and 500 nanograms.

### Site Evaluation

We have also developed unique sample preparation methodologies and portable TLC kit technologies for rapid field screening and quantitative assessment of explosives in the environment or in propellants (Figure 3). Indicative descriptors are logged throughout the analysis process, ensuring efficiency a higher level of confidence in the reporting of data. Some of the common observations to log are; date, time, conditions, names, and assignment of team members, GPS location, etc. Sample observations are sample sketch, sample type, GPS location of sample, quantity of sample retrieved, sampling method and equipment used. Unusual conditions, difficulties in collection, weather; topography, arctic, jungle, desert, etc. are noted.



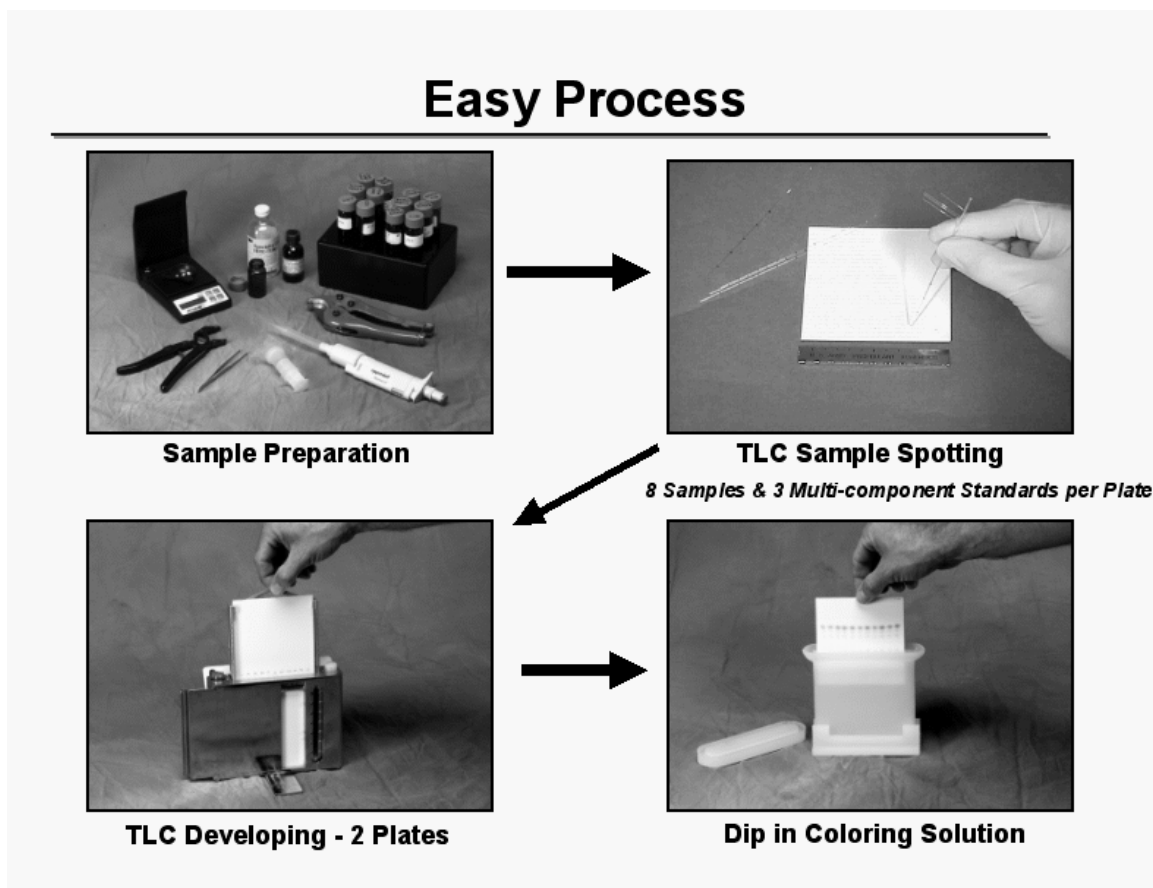
**Figure 3**

### Sample Quantity to Collect

The sample quantities to be collected should be sufficient for a replicate analysis. However, alternative plans for sampling can be implemented. For example, a homogenized sample can be divided for on-site analysis, archival, and also to have a portion sent for orthogonal analysis to an off-site lab.

### Chain of custody

Maintaining a chain-of-custody is necessary to ensure proper identification and tracking of each propellant sample from its collection to its analysis. The general procedure is to label samples, record in the sample collection logbook, and then upon transfer to the analyst, the analyst or recipient signs the collection logbook as well as the person releasing the sample. In the haste of an emergency collection scenario, chain-of-custody concerns tend to have low priority. However, sample tracking can be jeopardized and disorganized to the point of becoming a serious issue.



**Figure 3**

As shown in Figure 3, small (100-mg) propellant or soil samples are weighed on a portable battery operated balance and placed in 20-ml size vials for dissolution. The solvent system of choice for dissolution is an acetone and environmentally safe HFE 7100 made by 3M. Once the samples are processed, they are ready for TLC analysis.

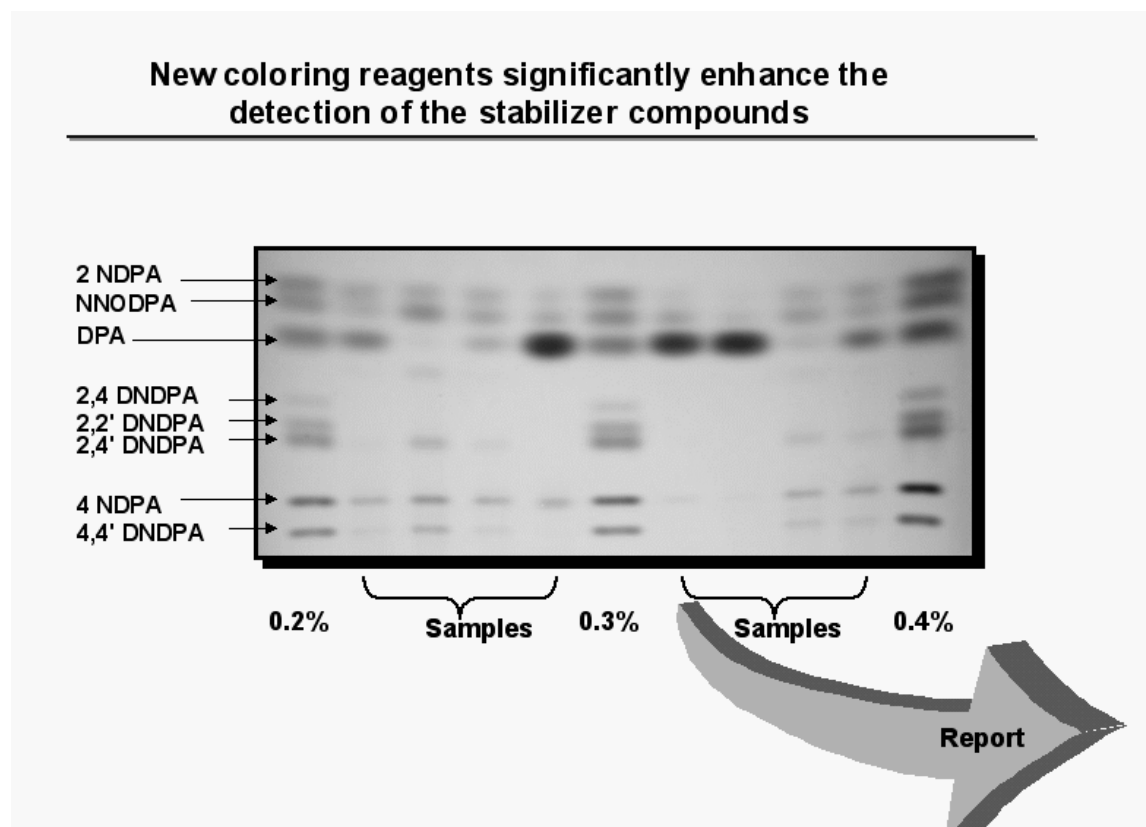
Pre-packaged, pre-marked TLC plates are then removed from the sealed plastic bag to which 5  $\mu$ L of each sample and standard are spotted. The concentration of the standards can represent calibration curves over large dynamic ranges or a more critical range close to the detection limits. Each prepackaged TLC plate has eight pre-marked sample locations and three pre-marked locations for standards.

One to two spotted TLC plates are positioned in a TLC rack, and then placed in a unique developing chamber containing a very small amount of solvent. The solvent wicks up the TLC plate, over and past the spotted propellant samples and standards. Chemical components from each spotted sample and standard begin to separate (i.e., chromatography) moving up the plate, and continue to different heights on the TLC plate.

Once the timed chromatographic process is over, the components (energetic materials and associated biodegradation and/or decomposition products) in each sample are then read directly as spots on the TLC plate. The spots are visualized as they fluoresce or cause fluorescent quenching under UV-lamp illumination, or the spots are chemically developed *in situ* using



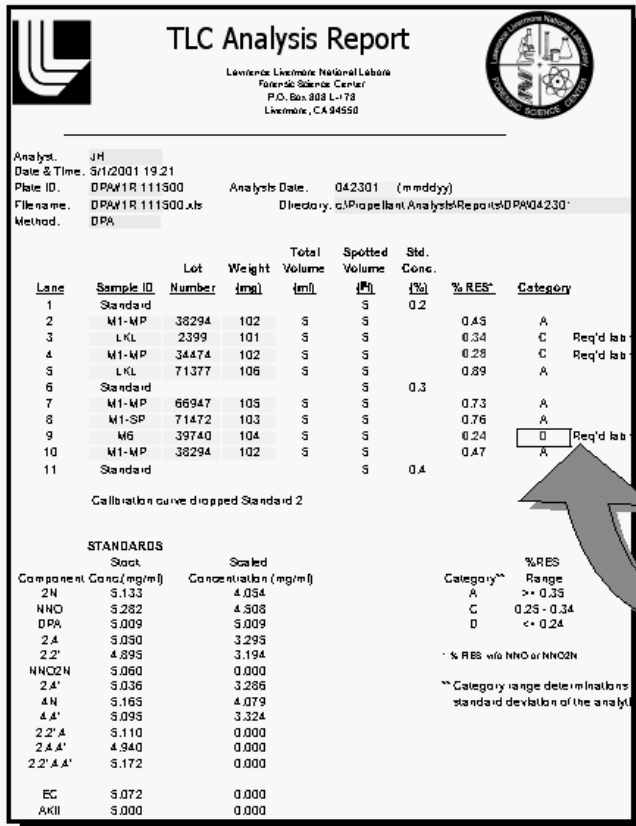
reagents unique to those analytes. As shown in Figure 4, the density and size of the spot are related directly to concentration. However, the visual semi-quantitation and/or quantitation of these separation data can be subjective because of random spot sizes and/or irregular shapes.



**Figure 4**

To increase the objectivity of reading TLC plates, we have designed a unique digital imaging box wherein lies the developed TLC plate. The digital imaging box is complete with UV and room light illumination capabilities and is fitted with a detachable digital camera. The imaged TLC plate is imported into a software program for data reduction.

Extracting the semi-quantitative/quantitative information from a TLC plate requires integration of spot density. The digital camera images (i.e., captures) very low-light spot intensities with three different color channels: red, yellow, and blue. The spots are imaged over time (1/60 of a second) and are conveniently stored on a floppy disk or smart stick and then downloaded directly into the computer. The software integrates the intensity volume for each imaged spot using the best color channel(s) combination and compares it to known standard compounds that were run with the samples on the same plate, thereby analyzing the sample. The propellant's stabilizer content is readily viewed on-screen or printed out in the final report (See Figure 5).



**Sample Disposition**

**Samples determined to be in category C or D levels will be sent off-site for HPLC**

**Figure 5**

A complete, highly detailed, sample preparation and analysis procedure is provided in the Operations Manual and is available.

### Summary

There was a need to develop field-portable, AC power independent, rugged sample collection and TLC kits that are cost-effective, and efficient for analyzing very large numbers of propellant samples per day for stabilizers and explosives on-site at military facilities.

Lawrence Livermore National Laboratory's (LLNL) Forensic Science Center (FSC), is continuing to develop, test, and incorporate state-of-the-art technologies for the portable TLC system. This year, we have further improved the accuracy and precision of the data by developing new technologies, new chemistries, and software analysis routines. The new TLC technology is in kit form and has been transitioned to Ho`olana Technologies, located in Hilo, Hawaii, for the manufacturing of future Army kits. This technology is now also directly applicable, for the rapid sampling and analysis for trace level detection of energetic materials in large numbers of environmental samples.

<p>This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.</p>
--